OH reactivity for screening crops volatiles

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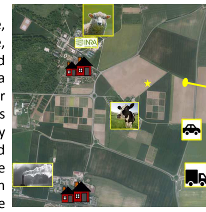
1. Goal of the study

Only a few studies of volatile organic compounds (VOCs) emissions from croplands are dated to exist [1]. Specifically, no field studies have been conducted so far on the emissions of the most diffused type of crop in Northern Europe, *winter wheat*. In order to determine the regional impact of emissions from croplands and land use changes we need to know the type, amount, direction of exchange of VOCs, as well as their total atmospheric reactivity. We measured the concentrations, fluxes and OH reactivity in a field of *winter wheat* in Northern France during June 2016. The total OH reactivity is the first-order total loss rate of the hydroxyl radical in the atmosphere due to reactive molecules[2]. In our study such value is measured and will be compared to the summed reactivities from the identified VOCs, to quantify the budget of known VOCs.

2. Field site

Our field site is located in the countryside, 40 km West of Paris (France, 45° 39'4.09"N). The agricultural field consists of 20 ha of land managed with a crop rotation of: corn, winter wheat, winter barley, mustard since 2000. The cropland is surrounded by a farm (which houses dairy cattle and a methaniser), other cultivated fields, towns (~1000 inhab.) and roads. The culture of this year was winter wheat, with a LAI of the field of 3.29, and average height during June 2016 of about 1 m.

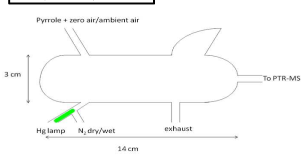


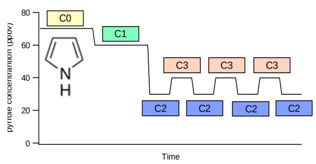
3. Methods

(1) MEASURED TOTAL OH REACTIVITY:
Comparative Reactivity Method (CRM): glass flow reactor+ PTR-MS [3]

A known amount of a reference molecule (pyrrole, C_4H_5N) is alternatively diluted in clean air and ambient air and introduced into a glass flow reactor where OH is produced through photolysis of water vapour at 185 nm. A proton transfer reaction- mass spectrometer monitors the concentration of pyrrole while this competes for OH radicals with ambient reactants. The LOD of this instrument is ~3 s^{-1} and the uncertainty is 35%.

$$R = \frac{(C3-C2)}{(C1-C3)} \cdot Kp \cdot C1$$





(2) CALCULATED OH REACTIVITY:
Summed OH reactivity of measured reactive gases:

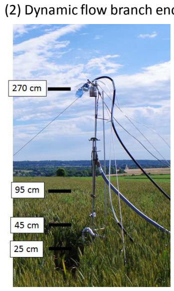
T heated box with manifold for sampling lines

PTR-Qi-TOF

QCL, IR absorption, chemiluminescence

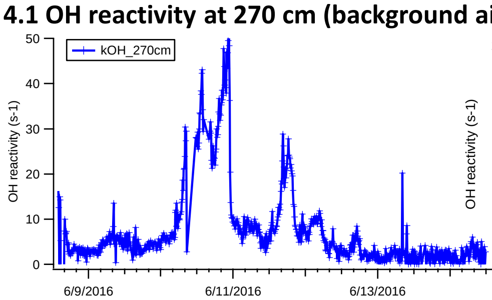
$$R = \sum_i k_{i+OH} \cdot X_i$$

HOW:
(1) Concentrations of VOCs and OH reactivity profiles within and above the field
(2) Dynamic flow branch enclosure system

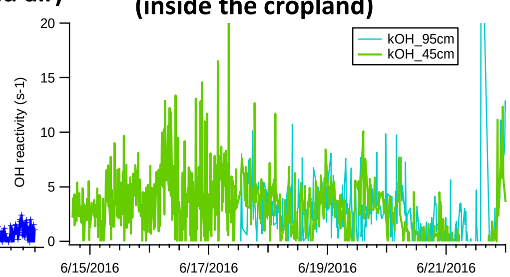


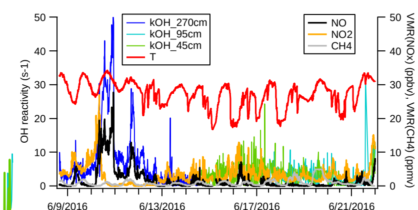
4. Preliminary results

4.1 OH reactivity at 270 cm (background air)



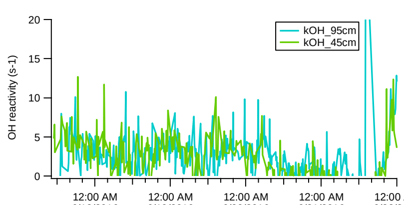
4.2 OH reactivity at 45 cm (inside the cropland)



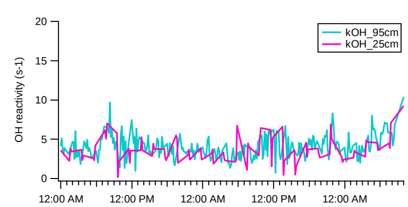


The OH reactivity measured at 270 cm and at 45 cm was maximum 50 s^{-1} and 20 s^{-1}, respectively. In both cases we expect a significant influence of background air components mainly from anthropogenic sources (traffic, methane producer inside the farm and farm) nearby the field site.

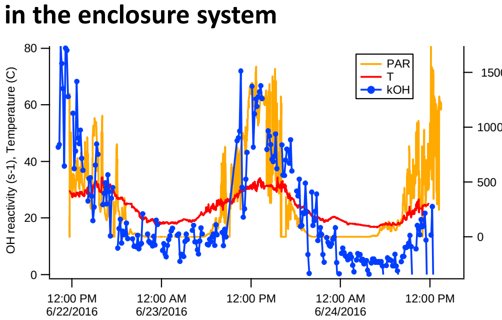
4.3 Profiles of OH reactivity: 45-95 cm; 25-95 cm



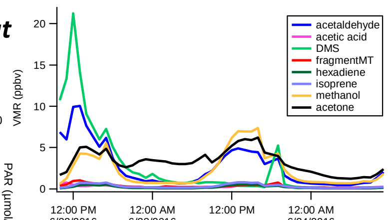
Preliminary results of OH reactivity measured inside the cropland suggest that no large amount of reactive species are emitted by winter wheat at the ambient conditions encountered during our field campaign, neither at 45 cm, nor at 25 cm. Profile results indicate that no significant difference in OH reactivity is measured within the investigated heights (height of the crop during June 2016 about 1m).

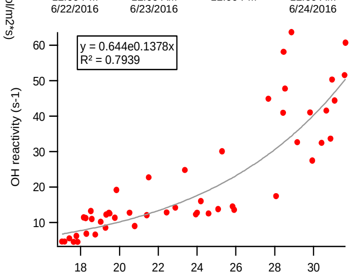


4.4 OH reactivity and VOCs of *winter wheat* in the enclosure system



The OH reactivity of *winter wheat* enclosed inside a dynamic chamber peaked at 80 s^{-1} (just after the installation) and 60 s^{-1} at midday. It varies with temperature and PAR, suggesting the influence of emissions of oxygenated molecules and terpenes. Preliminary analysis of data from PTR-TOF-MS indicate the emissions of many biogenic and oxygenated molecules (biomass of wheat enclosed 46.2 g).





5. Conclusion and Perspectives

- The OH reactivity measured above a winter wheat field in North-West Europe at the ambient conditions of summer 2016 peaked during some anthropogenic events, otherwise was about the limit of detection of our instrument., suggesting that wheat is a weak VOCs emitter.
- No significant difference in OH reactivity was encountered at different heights of the cropland.
- The OH reactivity of *winter wheat* ears enclosed in a dynamic chamber varies with PAR and temperature. It has a temperature dependence similar to oxygenated molecules and terpenes.
- Preliminary VOCs analysis from PTR-MS data suggest the presence of many species, mostly oxygenates.
- Analysis of VOCs data will be used to calculate the OH reactivity and analyse the reactants budget.
- Perspective studies of crops in pots as well as rapeseed at ambient conditions will help determining the VOCs emitted by crops and their atmospheric influence.

Acknowledgments

This work was supported by ADEME (program CORTEA-COV3ER), CEA, CNRS and UVSQ. R. Sarda-Estève, D. Baisnée, B. Bonsang, J.-C. Geudet, O. Zurfluh, O. Fanucci and B. Durand are acknowledged for helping with the experiments.

[1] Bachy A., et al.: Are BVOC exchanges in agricultural ecosystems overestimated? Insights from fluxes measured in a maize field over a whole growing season, Atmos. Chem. Phys., 16, 5343-5356, 2016.
[2] Kovacs, T. A. and Brune, W. H.: Total OH Loss Rate Measurement, J. Atmospheric Chem., 39(2), 105–122, doi:10.1023/A:1010614113786, 2001.
[3] Sinha et al., *The Comparative Reactivity Method-a new tool to measure total OH reactivity in ambient air.* Atmos. Chem. Phys., 8, 2213-2227, 2008.